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Note

Reactivity of cationic decamethylmetallocene complexes towards ketones

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ABSTRACT

Reaction of decamethylmetallocene cations $[\text{Cp}^*_2\text{M}]^+$ ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$) with acetone and benzophenone resulted in the formation of the corresponding acetone adducts $[\text{Cp}^*_2\text{M}(\text{OCMe}_2)_n]^+$ ($\text{M} = \text{Sc}, n = 2$; $\text{M} = \text{Ti}, n = 1$; $\text{M} = \text{V}, n = 1$) and benzophenone adducts $[\text{Cp}^*_2\text{M}(\text{OCPh})]^+$. The stoichiometry of these adducts is determined by both the electronic configuration of the metal center as well as steric pressure imparted by the large Cp^* -ligands. In addition, the $\text{M}-\text{O}-\text{C}$ angle is controlled by the number of free valence orbitals of the Cp^*_2M unit.

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1. Introduction

Early transition metal complexes play an important role in the (selective) transformation of ketones [1], such as the reduction [2], hydrosilylation [3], olefination [4], the addition of metal-alkyl fragments [5], the Aldol condensation [6] and the reductive coupling to form diols (pinacol coupling) [7]. It is expected that the initial step in these transformations is the coordination of the substrate via oxygen. It is known, that ketones can bind to early transition metals in different ways, depending on the metal center, ranging from κO -bound adducts [8], to side-on bound η^2 -ketone complexes [7b,9] and dimeric structures [10].

We have been interested in the coordination chemistry of cationic decamethylmetallocene cations of trivalent metal centers [11]. Here we describe the reactivity of $[\text{Cp}^*_2\text{M}][\text{BPh}_4]$ ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$) with acetone and benzophenone to probe the influence of the electronic structure of the metallocene fragment on the coordination mode of the ketone ligand.

2. Experimental section

2.1. Materials and methods

All reactions and manipulations of air and moisture sensitive compounds were performed under a nitrogen atmosphere using

standard Schlenk, vacuum line, and glovebox techniques. Reagents were purchased from commercial suppliers and used as received, unless stated otherwise. THF- d_8 and cyclohexane were dried over Na/K alloy prior to use and THF was dried by percolation over columns of aluminum oxide, BASF R3-11 supported Cu oxygen scavenger, and mol. sieves (4 Å). $[\text{Cp}^*_2\text{M}][\text{BPh}_4]$ ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$) were prepared according to literature procedures [11]. ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonances. IR spectra of KBr pellets of the samples were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. Despite many attempts we were not able to obtain satisfactory elemental analysis data because of low, but reproducible, carbon values. This is a common observation for organometallic complexes with a high carbon content and is associated with the formation of inert carbide species [11]. In all cases, V_2O_5 was added to the samples to reduce the formation of such species.

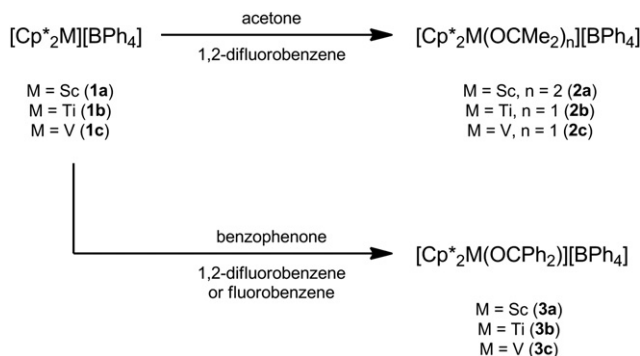
2.2. Preparation of $[\text{Cp}^*_2\text{M}(\text{OCMe}_2)_n][\text{BPh}_4]$ ($\text{M} = \text{Sc}, n = 2$; $\text{M} = \text{Ti}, n = 1$; $\text{M} = \text{V}, n = 1$)

Metallocene cations $[\text{Cp}^*_2\text{M}][\text{BPh}_4]$ were dissolved in 1,2-difluorobenzene. To the resulting solutions a small excess of acetone was added. Recrystallization from 1,2-difluorobenzene/cyclohexane resulted in small amounts of single crystals of the corresponding acetone adducts. No attempts were made to optimize the yields. $[\text{Cp}^*_2\text{Sc}(\text{OCMe}_2)_2][\text{BPh}_4]$: ^1H NMR (THF- d_8 , RT, 200 MHz) δ 7.31 (br, $\Delta\nu_{1/2}$ 15 Hz, BPh_4), 6.87 (t, 7.2 Hz, BPh_4), 6.72 (t, 7.2 Hz, BPh_4), 2.38 (br, $\Delta\nu_{1/2}$ 15 Hz, OCMe_2), 1.79 (s, Cp^*) ppm. $[\text{Cp}^*_2\text{Ti}(\text{OCMe}_2)][\text{BPh}_4]$: IR (KBr pellet) 3051(s), 3031(s), 2996(s),

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Scheme 1. Synthesis of acetone adducts **2a–c** and benzophenone adducts **3a–c**.

2980(s), 2963(s), 2902(s), 2859(m), 1665(s), 1579(m), 1478(s), 1426(s), 1378(s), 1355(m), 1264(w), 1254(m), 1181(w), 1143(m), 1065(m), 1029(m), 1019(m), 909(w), 859(w), 844(m), 802(w), 734(s), 705(s), 624(w), 606(s), 533(w), 482(w), 461(m), 414(w) cm^{-1} . $[\text{Cp}^*_2\text{V}(\text{OCMe}_2)][\text{BPh}_4]$: IR (KBr pellet) 3025(s), 3031(m), 2997(m), 2982(m), 2963(m), 2920(s), 2851(w), 1744(w), 1672(s), 1582(m), 1479(s), 1448(w), 1426(s), 1381(m), 1356(w), 1321(m), 1281(m), 1262(s), 1183(w), 1151(w), 1128(w), 1068(s), 1019(s), 887(w), 844(w), 801(m), 733(s), 706(s), 663(w), 639(w), 606(m), 527(w), 466(w), 414(w) cm^{-1} .

2.3. Preparation of $[\text{Cp}^*_2\text{M}(\text{OCPh}_2)][\text{BPh}_4]$ ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$)

Metallocene cations $[\text{Cp}^*_2\text{M}][\text{BPh}_4]$ were dissolved in fluorobenzene ($\text{M} = \text{Sc}$) or 1,2-difluorobenzene ($\text{M} = \text{Ti}, \text{V}$). To the resulting solutions a small excess of benzophenone was added. Recrystallization by slow diffusion of cyclohexane into these solutions resulted in small amounts of single crystals of the corresponding benzophenone adducts. No attempts were made to optimize the yields. $[\text{Cp}^*_2\text{Sc}(\text{OCPh}_2)][\text{BPh}_4]$: ^1H NMR ($\text{THF}-d_8$, RT, 200 MHz) δ 7.76 (d, 6.8 Hz, OCPh_2), 7.63 (d, 7.4 Hz, OCPh_2), 7.51 (t, 7.4 Hz, OCPh_2), 7.3 (br, BPh_4), 6.84 (t, 7.6 Hz, BPh_4), 6.69 (t, 6.9 Hz, BPh_4), 1.91 (s, Cp^*) ppm. IR (KBr pellet) 3054(s), 3032(s), 3000(s), 2998(s), 2947(s), 2908(s), 2898(s), 2872(s), 2859(s), 1656(w), 1605(s), 1585(s), 1554(s), 1480(w), 1447(m), 1425(w), 1381(w), 1324(s), 1292(s), 1280(m), 1182(w), 1159(w), 1064(w), 1029(w), 999(w), 940(w), 921(w), 842(w), 808(w), 770(w), 734(m), 703(w), 635(m), 614(w), 471(w) cm^{-1} . $[\text{Cp}^*_2\text{Ti}(\text{OCPh}_2)][\text{BPh}_4]$: IR (KBr pellet) 3054(s), 3000(s), 2982(s), 2920(s), 2908(s), 2850(s), 1657(w), 1618(w), 1581(m), 1544(m), 1505(m), 1482(w), 1446(m), 1526(m), 1380(w), 1327(m), 1289(w), 1266(m), 1203(w), 1182(w), 1152(w), 1100(w), 1065(m), 1023(m), 999(w), 942(w), 925(w), 842(w), 807(w), 748(m), 733(m), 703(s), 636(w), 612(w), 566(w), 546(w), 450(w), 413(w) cm^{-1} .

2.4. Crystal data

Crystals with suitable dimensions were mounted on top of a glass fiber, by using glovebox techniques and aligned on a Bruker

[12] SMART APEX CCD diffractometer. The final unit cell was identified, the structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF [13]. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis of **2a–c** resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined.

In the case of the benzophenone adducts, refinement was complicated by disorder problems. In the case of compound **3a** one of the co-crystallized mono-fluorobenzene solvent molecules was disordered over a rotation of 120° . The electron density of the F-atom appeared to be spread out, indicating rotational disorder. A disorder model (50:50 for F:H on both positions: bonded to C41 and C43) was used in the final refinement. The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp^2 or sp^3 hybridization at the C-atom as appropriate with $U_{\text{iso}} = c \times U_{\text{equiv}}$ of their parent atom, where $c = 1.2$ for the aromatic/non-methyl hydrogen atoms and $c = 1.5$ for the methyl hydrogen atoms and where values U_{equiv} are related to the atoms to which the hydrogen atoms are bonded. The methyl groups were refined as rigid groups, which were allowed to rotate free. In **3b** both difluorobenzene solvent molecules were rotational disordered by 60° and 120° . The atoms connected to C31 and C33 of one fluorobenzene molecule and to C41, C42, C43 and C44 of the other have a site occupancy factor of 0.5 (meaning in the average disorder 0.5 F and 0.5 H is bonded to each involved carbon). The hydrogen atoms were included in the final refinement riding on their carrier atoms similar to **3a**. In compound **3c** unrealistic displacement parameters were observed suggesting some degree of dynamic disorder, which is in line with the weak scattering power of the crystals investigated (dynamic means that the smeared electron density is due to fluctuations of the atomic positions within each unit cell). This dynamic behavior is especially seen in the positions concerning the cyclohexane molecule, which is located over an inversion center. The hydrogen atoms were included similar to compounds **3a**.

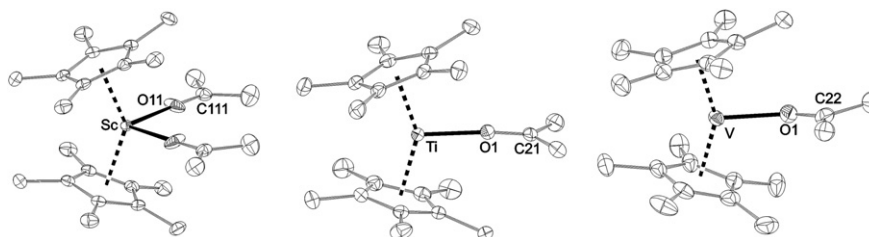


Fig. 1. ORTEP representation of the cation of **2a–c** showing 50% probability ellipsoids. The anions are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) of the cations of **2a–c**.

	2a	2b	2c
M(1)–Cp*(1) ^a	2.1895	2.0285	1.9566
M(1)–Cp*(2) ^b		2.0429	1.9710
M(1)–O(n1) ^c	2.1380(12)	2.0056(10)	2.0584(13)
O(n1)–C(m1) ^d	1.2248(19)	1.2330(17)	1.225(2)
Cp*(1)–M(1)–Cp*(2)	139.71	146.24	148.67
M(1)–O(n1)–C(m1)	176.46(11)	173.47(9)	141.66(13)
O(n1)–M(1)–O(n1a)	91.50(5)		
Σ{angles M(1)} ^e		359.98	359.35
Σ{angles C(m1)} ^f	359.9(3)	360.0(2)	359.9(3)
∠(Cp* ₂ M, MO ₂) ^g	89.11		

^a Cp*(1) is the centroid of the C(11)–C(15) ring (M = Sc, V) or C(1)–C(5) ring (M = Ti).

^b Cp*(2) is the centroid of the C(11)–C(15) ring (M = Ti) or C(111)–C(115) ring (M = V).

^c M = Sc, V: *n* = 1; M = Ti, *n* = 0.

^d M = Sc: *m* = 11; M = Ti: *m* = 2; M = V: *m* = 12.

^e Σ{angles M(1)} is defined as the sum of the angles around M(1).

^f Σ{angles C(m1)} is defined as the sum of the angles around C(m1).

^g ∠(Cp*₂M, MO₂) is defined as the angle between the Cp*(1)–M(1)–Cp*(1a) and O(11)–M(1)–O(11a) plane.

Final refinement on F^2 carried out by full-matrix least-squares techniques. The final difference Fourier map was essentially featureless: no significant peaks having chemical meaning above the general background were observed. The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum h[w(|(F_o^2) - k(F_c^2)|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$, F_o and F_c are the observed and calculated structure factor amplitudes, respectively; ultimately the suggested *a* and *b* were used in the final refinement.

Compound 2a: C₅₀H₆₂BO₂Sc, FW = 750.81, monoclinic, space group C2/c, *a* = 20.539(1), *b* = 28.090(2), *c* = 15.3825(9) Å, β = 104.467(1)°, *V* = 8593.4(9) Å³, *Z* = 8, d_{calc} = 1.161 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 2.09 cm^{−1}, *T* = 100(1) K, θ range: 2.40°–27.50°. *wR* (F^2) = 0.1118 (reflections: 9831, parameters: 736). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0425, weighing (*a*, *b*) = 0.0567, 2.69.

Compound 2b: C₄₇H₅₆BO₂Ti, FW = 695.64, monoclinic, space group P21/n, *a* = 10.3560(5), *b* = 32.500(2), *c* = 11.8554(5) Å, β = 92.960(1)°, *V* = 3984.8(4) Å³, *Z* = 4, d_{calc} = 1.160 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 2.48 cm^{−1}, *T* = 100(1) K, θ range: 2.33°–29.72°. *wR* (F^2) = 0.1163 (reflections: 10568, parameters: 675). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0449, weighing (*a*, *b*) = 0.060, 1.538.

Compound 2c: C₄₇H₅₆BO₂V, FW = 698.67, monoclinic, space group P21/c, *a* = 10.2905(6), *b* = 19.707(1), *c* = 19.210(1) Å, β = 96.4870(10)°, *V* = 3870.7(4) Å³, *Z* = 4, d_{calc} = 1.199 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 2.91 cm^{−1}, *T* = 100(1) K, θ range: 2.24°–29.75°. *wR* (F^2) = 0.1363 (reflections: 10083, parameters: 675). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0497, weighing (*a*, *b*) = 0.0805, 1.0278.

Compound 3a: C₆₉H₇₀BF₄O₂Sc, FW = 1009.08, monoclinic, space group P21/c, *a* = 9.9383(8), *b* = 31.438(3), *c* = 18.118(2) Å, β = 103.005(2)°, *V* = 5515.6(9) Å³, *Z* = 4, d_{calc} = 1.215 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 1.84 cm^{−1}, *T* = 100(1) K, θ range: 2.20°–27.32°. *wR* (F^2) = 0.1501 (reflections: 9726, parameters: 686). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0667, weighing (*a*, *b*) = 0.0362, 1.0517.

Compound 3b: C₆₉H₆₈BF₄O₂Ti, FW = 1047.97, monoclinic, space group P21/c, *a* = 9.9560(8), *b* = 31.273(3), *c* = 18.379(2) Å, β = 103.463(2)°, *V* = 5565.1(9) Å³, *Z* = 4, d_{calc} = 1.251 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 2.11 cm^{−1}, *T* = 100(1) K, θ range: 2.24°–25.03°. *wR* (F^2) = 0.1957 (reflections: 9797, parameters: 722). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0711, weighing (*a*, *b*) = 0.0793, 3.1460.

Compound 3c: C₁₂₃H₁₃₁B₂FO₂V₂, FW = 1783.90, triclinic, space group P-1, *a* = 10.4140(8), *b* = 20.749(2), *c* = 23.141(2) Å, α = 85.066(2)°, β = 81.545(2)°, γ = 88.534(2)°, *V* = 4929.3(7) Å³, *Z* = 2, d_{calc} = 1.202 g/cm³, $\mu(\text{Mo-K}\alpha)$ = 2.44 cm^{−1}, *T* = 100(1) K, θ range: 2.23°–19.5°. *wR* (F^2) = 0.1681 (reflections: 17180, parameters: 1191). *R*(*F*) for $F_o > 4.0 \sigma$ (F_o) = 0.0691, weighing (*a*, *b*) = 0.0598, 0.0.

2.5. DFT calculations

All calculations were carried out with the Turbomole program [14a,b] coupled to the PQS Baker optimizer [15]. Geometries were fully optimized at the bp86 [16]/R1DFT [17] level using the Turbomole SV(P) basis set [14c,d] on all atoms (small-core pseudopotential [14c,e] on Sc, Ti and V). The energies are relative to the base-free metallocene cations and do not include zero-point energies or thermal corrections. Furthermore, the anions have been omitted.

3. Results and discussion

3.1. Synthesis

The addition of an excess of acetone to 1,2-difluorobenzene solutions of decamethylmetallocene complexes [Cp*₂M][BPh₄] (M = Sc: **1a**, Ti: **1b**, V: **1c**) resulted in formation of the corresponding acetone adducts (**2a–c**, Scheme 1). The stoichiometry observed in these adducts is the same as found for the corresponding THF adducts we reported earlier [11]. Thus, in case of scandium a bis-acetone adduct is formed, whereas one molecule of acetone is bound in the case of titanium and vanadium. The analogous reaction of the base-free decamethylmetallocene cations with benzophenone resulted in the formation of the mono-benzophenone adducts, [Cp*₂M(OCPh₂)] [BPh₄] (**2a–c**, Scheme 1).

3.2. Structure

Acetone adducts **2a–c** were studied using single-crystal X-ray diffraction. The asymmetric unit of [Cp*₂Sc(OCMe₂)₂][BPh₄] consists of two crystallographically independent, but geometrically indistinguishable scandocene cations, each situated on a crystallographic

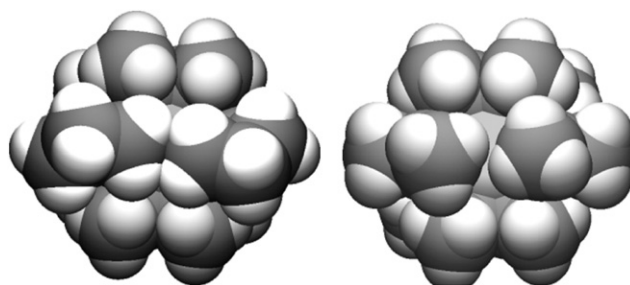


Fig. 2. Space filling models of the front view of [Cp*₂Sc(THF)₂]⁺ (left) and the cation of **2a** (right).

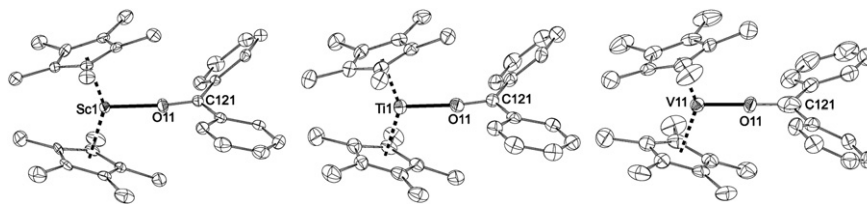


Fig. 3. ORTEP representation of the cation of **3a–c** showing 50% probability ellipsoids. The anions are omitted for clarity.

Table 2

Selected bond distances (Å) and angles (°) of the cations of **3a–c**.

	3a	3b	3c
M(1)–Cp*(1) ^a	2.1325	2.039	1.9725
M(1)–Cp*(2) ^b	2.1368	2.0400	1.980
M(1)–O(11)	2.051(2)	1.988(3)	1.820(3)
O(11)–C(121)	1.256(4)	1.259(5)	1.359(5)
Cp*(1)–M(1)–Cp*(2)	145.52(7)	144.25(8)	140.92(8)
M(1)–O(11)–C(121)	174.4(2)	174.1(3)	176.9(3)
Σ{angles M(1)} ^c	360.00	360.00	360.00
Σ{angles C(121)} ^d	360.1(5)	360.0(6)	360.0(7)

^a Cp*(1) is the centroid of the C(11)–C(15) ring.

^b Cp*(2) is the centroid of the C(111)–C(115) ring.

^c Σ{angles M(1)} is defined as the sum of the angles around M(1).

^d Σ{angles C(121)} is defined as the sum of the angles around C(121).

C₂-axis, and of one [BPh₄][−] anion. ORTEP representations of the cations of **2a–c** are depicted in Fig. 1 (Table 1 consists of selected bond distances and angles). The geometry of the acetone adducts closely resembles that of the corresponding THF adducts [11]. The Cp*–M–Cp* angles are slightly larger (acetone adducts: M = Sc, 139.71°; M = Ti, 146.24°; M = V, 148.67°; THF adducts: M = Sc, 137.21°; M = Ti, 142.11°; M = V 146.51°) and the O–M–O angle in **2a** (91.50(4) deg) is virtually identical to that in [Cp*₂Sc(THF)₂][BPh₄] (91.59(5)°). The Cp*–M and the M–O bond distances in **2a–c** are shorter than the corresponding distances in the THF adducts. This might be a result of the fact that in the acetone molecule the methyl groups are more distant from the metal compared to the α -methylene moieties of the THF ligand. Therefore, the acetone ligands are less affected by steric bulk imparted by the large Cp*–ligands (Fig. 2). The Ti–O bond distance in **2a** is shorter compared to that in [Cp₂Ti(OCMe₂)(THF)]⁺ [8a], as expected considering the lower coordination number of the metal center in **2a**. The V–O bond distance in **2c** of 2.0584(13) Å is smaller than that in [Cp₂V(OCMe₂)]⁺ (2.081(4) Å) [8b]. The C=O bond distance of the acetone molecule is virtually unaffected by the coordination to the transition metal ions (M = Sc: 1.2248(19); M = Ti: 1.2330(17); M = V: 1.225(2) Å; free acetone:

1.218(3) and 1.221(3) Å [18]) and is in the range of other κ O-acetone adducts (1.212–1.269 Å) [8]. The most interesting structural feature of these acetone adducts is the M–O–C bond angles. In the case of **2a** and **2b** this angle is close to linear (176.46(11) and 173.47(9) deg respectively), whereas the corresponding angle in **2c** is significantly smaller (141.66(13)°). This suggests a correlation between the number of free valence orbitals on the metal and the M–O–C bond angles (linear vs. bent). In the case of complexes where the acetone ligand can donate more than one pair of electrons to the metal center (**2a**, **b** and **3a**, **b**) a linear M–O–C angle is observed. For compound **2c**, where only one free valence orbital is available for the interaction with ketone, a bent coordination mode is observed. This hypothesis is supported by observations made in the structure of the titanocene cation [Cp₂Ti(OCMe₂)(THF)][Zn(B₁₀H₁₂)₂] [8a] and the Zwitterionic [CpB(C₆F₅)₂(C₆F₅- κ F)]CpTi(OCMe₂) [8e]. In these complexes, one molecule of acetone and one additional donor ligand is bound to the metal center. Consequently, there is one valence orbital available for the interaction with the acetone ligand, similar to **2c**, thus bent M–O–C bond angles are observed (140.7 and 143.2(2) deg, respectively).

ORTEP representations of the benzophenone adducts **3a–c** can be found in Fig. 3 (Table 2 for selected bond distances and angles). Compounds **3a** and **3b** are isomorphous, and have virtually identical geometries, taking into account the difference in ionic radius of Sc³⁺ and Ti³⁺ [19]. The M–O bond distance in benzophenone adduct [Cp*₂Ti(OCPh₂)]⁺ is similar to that in the corresponding acetone adduct **2b** (1.988(3) vs. 2.0056(10) Å). This distance in **3a** is significantly shorter than that in the bis-acetone adduct of scandium (2.051(2) vs. 2.1380(12) Å), in response to the lower coordination number of the metal in **3a**. The M–O–C angles in **3a**, **b** are comparable to that in the corresponding acetone adducts, i.e. close to linear. The [Cp*₂V(OCPh₂)] cation also adopts a bent metallocene geometry with a linear V–O–C bond angle of 176.9(3)°, instead of a bent V–O–C angle as observed in the analogous acetone adduct **2c** (141.66(13)°). Unfortunately, we are uncomfortable in discussing the bond distances in the molecule as we have observed some

Table 3

Calculated binding energies (kcal/mol) for the acetone and benzophenone ligands including M–O bond distances and M–O–C bond angles^a.

	$E_{\text{rel}}^{\text{a}}$ kcal/mol	M–O (Å) calcd	X-ray	C–O (Å) calcd	X-ray	M–O–C (°) calcd	X-ray
[Cp ₂ Sc(OCMe ₂)] ⁺	−42.73	2.10	2.08	1.25	1.22	178.5	136.8
[Cp ₂ Sc(OCMe ₂) ₂] ⁺	−70.04	2.16, 2.15		1.24, 1.24		159.1, 164.0	
[Cp ₂ Ti(OCMe ₂)] ⁺	−42.04	2.03		1.25		178.9	
[Cp ₂ V(OCMe ₂)] ⁺	−37.20	2.09		1.25		142.6	
[Cp ₂ Sc(OCPh ₂)] ⁺	−48.49	2.06		1.27		178.0	
[Cp ₂ Ti(OCPh ₂)] ⁺	−47.73	2.00		1.27		178.8	
[Cp ₂ V(OCPh ₂)] ⁺	−40.95	2.03		1.26		177.5	
[Cp* ₂ Sc(OCMe ₂)] ⁺	−34.04	2.10		1.25		178.2	
[Cp* ₂ Sc(OCMe ₂) ₂] ⁺	−52.40	2.15, 2.15	2.14	1.24, 1.24	1.22	177.9, 177.6	176.5
[Cp* ₂ Ti(OCMe ₂)] ⁺	−32.29	2.03	2.01	1.25	1.23	176.0	173.5
[Cp* ₂ V(OCMe ₂)] ⁺	−22.94	2.08	2.06	1.24	1.23	151.8	141.7
[Cp* ₂ Sc(OCPh ₂)] ⁺	−36.84	2.08	2.05	1.27	1.26	179.3	174.4
[Cp* ₂ Ti(OCPh ₂)] ⁺	−34.76	2.01	1.99	1.27	1.26	178.1	174.1
[Cp* ₂ V(OCPh ₂)] ⁺	−23.81	2.06	1.82	1.26	1.36	178.9	176.9

^a Binding energy listed are relative to [Cp*₂M]⁺.

unrealistic C–C bond distances in the structure of **3c**: the C–Ph bond distances observed are 1.58–1.60 Å (1.47 Å for compounds **3a**, **b**).

3.3. Computational studies

To probe the preferred binding modes of acetone and benzophenone to these trivalent decamethylmetallocene cations, both the acetone and the benzophenone adducts were studied using RIDFT calculations (see [Experimental Section](#) for more information on the calculations, and [Table 3](#) for energies). In addition to the $[\text{Cp}^*_2\text{M}]$ ketone adducts, also the corresponding $[\text{Cp}_2\text{M}]$ complexes were considered. The optimized geometries are in general very similar to the X-ray data. The relative energies associated with the binding of acetone vs. benzophenone are very similar, especially in case of the $[\text{Cp}^*_2\text{M}]$ cations. Furthermore, the calculations corroborate the observation that the coordination of a second molecule of acetone is favored in case of **2a**. The binding energies in the scandocene and titanocene cations are virtually identical, whereas those in the vanadocene cations are considerable smaller.

4. Conclusions

The reaction of the decamethylmetallocene cations $[\text{Cp}^*_2\text{M}]$ $[\text{BPh}_4]$ ($\text{M} = \text{Sc}, \text{Ti}, \text{V}$) with ketones resulted in the formation of the corresponding κO -ketone adducts. The stoichiometry of the reactions is dependent on both electronic and steric factors. For acetone, complexes with the same stoichiometry were obtained as the corresponding THF adducts. In case of the larger benzophenone ligand, mono-benzophenone adducts were isolated, exclusively. In the absence of overruling steric effects, the $\text{M}—\text{O}—\text{C}$ angle in these ketone adducts is dependent on the number of free valence orbitals in the base-free metallocene cations. A bent coordination of the ketone is observed in case of complexes with one free valence orbital ($\text{M} = \text{V}$), whereas linear structures are observed when the ketone can donate more than one pair of electrons to the metal center ($\text{M} = \text{Sc}, \text{Ti}$). In the benzophenone adduct $[\text{Cp}^*_2\text{V}(\text{OCPh}_2)]^+$, a close to linear $\text{M}—\text{O}—\text{C}$ angle was observed as well. This is most likely the result of the increased size of the benzophenone ligand compared to the acetone ligand. The acetone and benzophenone ligands in the other complexes seem virtually unaffected by the binding to the metallocene cations.

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Appendix A. Supplementary material

CCDC 775892–775898 contain the supplementary crystallographic data for the X-ray structures in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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